

to form supersaturated solutions, and they become more sensitive to the action of nuclei as the temperature falls, or, in other words, as they become more highly supersaturated. Thus a very strong solution of calcic chloride, which is not sensitive to nuclei at 40° or 45°, becomes very much so at 24° to 34°.

The sodio-zincic sulphate contains only 4 proportionals of water of crystallization, and hence its supersaturated solutions are not stable at low temperatures. When freshly made, they may be reduced to 10° Fahr. without separation of the salt; but by repose, even in clean tubes and in the absence of nuclei, long crystals of the separated salts occupy the length of the tube, but they are invisible on account of having the same refractive index as that of the solution in which they are immersed. In the course of time, probably from the escape of vapour of water through the porous plug, they become visible.

A solution of the ammonia zincic sulphate at 4° Fahr. formed beautiful large feathery crystals of an opaque white, which gradually filled the tube. They melted rapidly at 32°.

A supersaturated solution of nickel sulphate resisted a temperature of 6° Fahr. Mixed with an equivalent weight of cupric sulphate, the two salts separate if the solution be exposed to the air, but in closed tubes the solution at 0° Fahr. forms beautiful feathery crystals, which melt rapidly at 32°, without any separation of salt.

Similar phenomena are produced by a supersaturated solution of zinc sulphate and potash alum in equivalent proportions exposed to a temperature of 4° Fahr. A similar solution of the cupric and magnesian sulphates at -4° also became solid, and melted rapidly at 32°.

Experiments were also made with the sodic and magnesian sulphates, cadmic, and some other sulphates. The addition of potassic sulphate to other sulphates, in atomic proportions, forms double salts, which, so far as they were examined, do not form supersaturated solutions.

The effect of low temperatures was in some cases to throw down a portion of the salts in the anhydrous form, upon which were formed by repose crystals of a lower degree of hydration than the normal salt. Some cases of this kind are described in the paper.

VIII. "On Furfuraniline and Furfurtoluidine." By JOHN STENHOUSE, LL.D., F.R.S. Received May 19, 1870.

In an epistolary communication to Mr. H. Watts * I stated that "The most abundant and economical source of furfural is in the preparation of garancin by boiling madder with sulphuric acid. If the wooden boilers, in which garancin is usually manufactured were fitted with condensers, furfural might be obtained in any quantity without expense. Furfural is

* Watts's Dictionary, ii. 751.

also produced by boiling any kind of madder with solution of sulphate of aluminium.

Crude furfural, whether obtained from madder, bran, sawdust, or any other of its usual sources, is always contaminated with another aromatic oil, which I called metafurfural*. This has a higher boiling-point, and oxidizes more readily than furfural, so that by repeated rectification almost the whole of it is converted into a brown resinous matter, which remains in the retort. It is owing to the presence of this impurity that crude furfural so rapidly changes its colour when kept, the metafurfural not only being itself decomposed, but superinducing the oxidation of the furfural.

A much simpler and more effective method, however, of purifying furfural from this substance consists in digesting it for some hours with very dilute sulphuric acid, to which small quantities of acid potassium chromate are added from time to time; this effectually destroys the metafurfural and other impurities, so that the furfural which distils over after being separated from the water and dried over fused chloride of calcium has a constant boiling-point of 161° C. It has a much more agreeable odour than before, is nearly colourless, and may be exposed to the air under a layer of water for months, without any considerable increase of colour. Its refractive index for the D line at 20° C. is 1.520 †.

Action of Furfural on Aniline Furfuraniline.

Twenty years ago ‡ I stated that when aniline was added to furfural, the mixture acquired a rose-red colour, which it communicated to the skin, and likewise to paper, linen, and silk, but that these rapidly lost their colour, becoming of a brownish yellow, even when light was excluded. I was unable, however, to obtain this red substance in a crystalline state.

In 1860 the subject was again examined by M. Jules Persor §, who dissolved aniline in acetic acid, and then added an excess of aqueous solution of furfural; after some time a deep red viscid mass was deposited on the sides of the vessel, which communicated to silk and wool a fine but very fugitive red colour. He was not more fortunate than I had been in obtaining this substance in a crystalline state.

A few months ago I resumed the investigation of this subject, and although I was unable to obtain definite compounds either by the action of furfural on aniline itself or on its salts when in a pure state, yet when furfural was added to a strong alcoholic solution of aniline hydrochlorate containing an excess of aniline a deep red colour was produced, and in the course of a few minutes the mixture solidified to a crystalline mass of a fine iridescent purple colour.

* Ann. Chem. Phar. lxxiv. 282.

† I am indebted to the kindness of Messrs. T. and H. Smith, of Edinburgh, for the greater portion of the furfural employed in this investigation. This firm has long been in the habit of manufacturing it for preparing furfurine for medical purposes.

‡ Ann. Chem. Pharm. lxxiv. 282.

§ Rep. Chem. App. 1860, p. 220.

Furfuraniline hydrochlorate.—The best method of preparing this salt was to dissolve 46 parts aniline and 65 parts aniline hydrochlorate in 400 parts of warm alcohol, and then add 48 parts furfurol, likewise dissolved in 400 parts spirit; after the solutions were thoroughly mixed, they solidified in the course of a few minutes to a mass of crystals of the salt. When cold, these were thrown on to a filter, freed from the mother liquor by means of a vacuum filter, and washed with a small quantity of coloured spirit. They were then readily obtained in a pure state by recrystallization from boiling spirit. The substance analyzed was dried *in vacuo*.

I. .207 grm. substance gave .488 grm. carbonic anhydride and .120 grm. water.

II. .158 grm. substance gave .372 grm. carbonic anhydride and .082 grm. water.

III. .228 grm. substance gave .103 grm. argentic chloride.

IV. .282 grm. substance gave .128 grm. argentic chloride.

V. .0448 grm. substance gave .003773 grm. nitrogen.

		Theory.	I.	II.	III.	IV.	V.	Mean.
C ₁₇ =	204	64.05	64.30	64.21				64.25
H ₁₉ =	19	5.97	6.44	5.77				6.10
O ₂ =	32	10.05						
N ₂ =	28	8.79					8.42	8.42
Cl =	35.5	11.14			11.18	11.23		11.20
		318.5						

This corresponds nearly to the formula C₁₇ H₁₈ O₂ N₂, Cl H.

It is insoluble in benzol, bisulphide of carbon, and water, but is slowly decomposed when boiled with the latter. It is soluble in boiling spirit, and crystallizes out on cooling in small needles of a fine purple colour, which acquire a metallic lustre on drying. The crystals are permanent in dry air when light is excluded, but are readily decomposed when boiled with dilute acids or alkalis.

Furfuraniline nitrate.—This is prepared in a manner similar to that employed for the hydrochlorate: 23 parts aniline and 39 of nitrate were dissolved in 200 parts warm spirit, and 24 parts furfurol in 200 of spirit added. The mixture, on being allowed to stand some time, became a semisolid crystalline mass, which was purified in the same manner as the corresponding hydrochlorate.

I. .289 grm. substance gave .628 grm. carbonic anhydride and .157 grm. water.

	Theory.	I.
C ₁₇ = 204	59.13	59.28
H ₁₉ = 19	5.51	6.04
N ₃ = 42	12.17	
O ₅ = 80	23.19	
345	100.00	

This nitrate is therefore $C_{17} H_{18} N_2 O_2, NO_3 H$.

It resembles the hydrochlorate in its properties, but is much more soluble in boiling spirit, and forms larger crystals.

Furfuraniline sulphate.—When 23 parts aniline and 35 of its sulphate were dissolved in 3000 of boiling alcohol, and 24 parts of furfural in 200 of boiling spirit added, the mixture became deep red, and on cooling deposited minute purple needles of the furfuraniline sulphate, contaminated, however, with colourless crystals of aniline sulphate. When an attempt was made to separate these by crystallization from alcohol, the furfuraniline salt was mostly decomposed, with formation of aniline sulphate, which crystallized out.

Furfuraniline oxalate.—When aniline oxalate of aniline and furfural were dissolved in spirit, as in the preparation of the salts above described, the solution became of a deep red colour, but did not yield crystals of oxalate of furfuraniline, only oxalate of aniline and a dark red tarry matter being produced.

Furfuraniline.—In order to obtain this base, a salt of furfuraniline (the hydrochlorate or nitrate) was ground up to a paste with water and strong aqueous ammonia added, the whole being intimately mixed until the purple colour disappeared, giving place to a pale brown. Warm water was then added until the liberated base became soft and plastic, so that it could be needed in successive quantities of warm water, in order to remove the ammoniacal salts and free ammonia. The base, as thus prepared, has much the pale brown glossy appearance of stick lac, and, like it, can be drawn out into strings when soft. It is insoluble in water, but very soluble in ether and alcohol, and when hydrochloric acid is added to a strong spirituous solution it becomes deep red, and solidifies in a few moments to a mass of the purple crystals of the hydrochlorate. The base decomposes, however, very rapidly when exposed to the air, or when boiled with alcohol, and will then no longer yield crystalline salts with acids. The same effect takes place, but more slowly, in a vacuum.

Action of Furfural on Toluidine Furfurtoluidine.

When alcoholic solutions of toluidine and furfural were mixed, there was no immediate change; but after standing some time they acquired a red colour: as in the corresponding reaction with aniline no crystalline substance was produced.

Furfurtoluidine hydrochlorate.—The method employed to obtain this salt was similar to that used in preparing furfuraniline hydrochlorate: 12 parts toluidine hydrochlorate and 9 parts crystalline toluidine were dissolved in 150 parts hot spirit, and 8 parts of furfural dissolved in 150 parts spirit added; the mixture acquired a deep-red colour, and on cooling became a mass of minute acicular crystals closely resembling in appearance the furfuralinine salt. It was purified by recrystallization from boiling alcohol, dried in vacuo, and analyzed.

I. .232 grm. substance gave .562 grm. carbonic anhydride and .135 grm. water.

	Theory.	I.
$C_{19} = 228$	65.80	66.07
$H_{23} = 23$	6.64	6.47
$O_2 = 32$	9.24	
$N_2 = 28$	8.08	
$Cl = 35.5$	10.24	
	346.5	100.00

This corresponds to $C_{19} H_{22} O_2 N_2, Cl H$.

Furfurtoluidine nitrate.—This was prepared in a manner similar to the hydrochlorate, substituting the equivalent proportion of toluidine nitrate: 14 parts toluidine nitrate and 9 parts toluidine were dissolved in 100 parts hot alcohol, and 8 parts furfurol in an equal quantity (100 parts) of spirit added; after standing some time the nitrate crystallized out in deep purple needles. When purified and analyzed it gave the following numbers:—

I. .160 grm. substance gave .355 grm. carbonic anhydride and .098 grm. water.

	Theory.	I.
$C_{19} = 228$	61.12	60.52
$H_{23} = 23$	6.17	6.81
$O_5 = 80$	21.45	
$N_3 = 42$	11.26	
	373	100.00

It has therefore the composition $C_{19} H_{22} N_2, NO_3, H$.

Furfurtoluidine.—The salts of furfurtoluidine, when treated with ammonia solution, were decomposed in a manner similar to that already described under the head *furfuraniline*, but not quite so readily. The crude free furfurtoluidine, when digested with ether, dissolved, and on filtering the solution, distilling off the ether, and drying the residue in a vacuum over sulphuric acid, the base was obtained as a brown amorphous mass, which is brittle and easily reduced to powder. It is not as fusible as furfuraniline, and is far less readily decomposed. A carbon and hydrogen determination of the freshly prepared base, purified by ether and dried *in vacuo*, gave the following results:—

I. .243 grm. substance gave .660 grm. carbonic anhydride and .159 grm. water.

	Theory.	I.
$C_{19} = 228$	73.54	74.08
$H_{22} = 22$	7.11	7.27
$O_2 = 32$	10.32	
$N_2 = 28$	9.03	
	310	100.00

This corresponds pretty nearly with the formula C_{19}, H_{22}, O_2, N_2 .

Both furfuraniline and furfuralidine resemble rosaniline in giving beautifully coloured salts, whilst the bases are nearly colourless, or of a pale brown colour.

Furfurnaphthylamine.—When an alcoholic solution of furfural was added to a similar solution of naphthylamine it immediately became of a red colour, which is as fugitive as the one obtained from aniline, but much duller. Several attempts were made to prepare crystalline salts of this compound, but without success, only dark-coloured resinous substances being obtained.

Several other typical bases were also tried, but without any results. These were quinidine, coniine, sparteine, and theine. It appears, therefore, from these experiments, that it is only the bases of the aromatic series which combine with furfural to yield these peculiar-coloured salts in a crystalline state.

I cannot conclude this paper without acknowledging the very efficient aid I have received from my assistant, Mr. Charles Edward Groves, in the preceding investigation.

IX. "On Parasulphide of Phenyl and Parasulphobenzine." By JOHN STENHOUSE, LL.D., F.R.S., &c. Received May 27, 1870.

When sulphide of phenyl, $\left. \begin{matrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{matrix} \right\} \text{S}$, was passed several times in succession through an iron tube filled with nails and heated to low redness, a considerable amount of carbonaceous matter was deposited, and a portion of the sulphide was converted into an isomeric compound, which I propose to call Parasulphide of Phenyl.

In order to obtain this substance from the dark-coloured distillate which collected in the receiver when sulphide of phenyl was submitted to the action of heat in the manner above described, it was transferred to a copper retort and distilled. The clear dark-yellow oil was then cooled for several hours in a freezing-mixture, when a considerable quantity of a white crystalline substance separated in nodules; this is freed from undecomposed sulphide of phenyl by thoroughly draining it on a vacuum filter. It can readily be purified by repeated crystallization from boiling alcohol, in which it is rather soluble.

I. .197 grm. substance gave .557 grm. carbonic anhydride and .092 grm. water.

II. .166 grm. substance gave .473 grm. carbonic anhydride and .077 grm. water.

III. .200 grm. substance gave .254 grm. barium sulphate.

IV. .218 grm. substance gave .276 grm. barium sulphate.